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Still needed data for successful deep CO_2 sequestration

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Abstract

Despite chemical knowledge about CO_2 that extends back centuries, some data bases are still evolving that are needed to predict even the sub-critical CO_2 behavior down the geothermal gradient's *P*- and *T*-values which will be encountered in sequestration utilizing deep mines and wells. These needed data include IR-spectral interpretations of CO_2 molecular structure as *P* and *T* change; the unraveling of the Joule Thomson coefficient (heating or cooling?) that changes algebraic polarity around 10^6 Pa; more exact equations of state (EOS) that correlate to potential CO_2 polarity changes in molecular structure; newer EOS than those that have currently been derived by templating directly measured data; and focus is needed on the EOS-derived properties, like fugacity. Also, natural analogues like (1) the carbonate stability in metamorphic silicate-carbonation facies and (2) Lake Nyos aqueous geochemistry with concern about the potential redox-equilibria-predicted presence of CO (and graphite), as well as CO_2.

Keywords: subcritical properties; molecular structure; equations of state; EOS; fugacity; IR-spectra; Joule Thomson coeffs.; redox.

1. Introduction

The purpose of this manuscript is to bring into focus the diversity of data on the properties of CO_2 . Some new data for carbon dioxide are being evolved in many international labs and many of the existing, even sub-critical pressure range data, are buried in 'unlikely' facets of the literature. Hence, this manuscript is intended to be a helpful outline to the plethora of data that exists and also the data that are still being sought. It seeks to help make more positive the efforts for successful sequestration. The role of CO_2 in wine and cheese and baking likely goes back more than one millennia in monastic recipes. However, the first documented reports (~1756) of its exact chemical properties are ascribed to the Scottish chemist, Joseph Black. [1, as reported in MJA].

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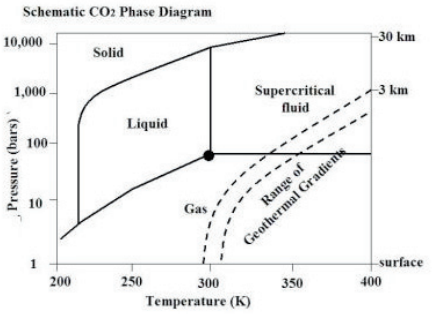
2. Equations of State (EOS) for the sub-critical behavior of CO_2 Gas

A review of the predictability of CO_2 gas in sub-critical pressure regimes has been shown by Marini (2007) [6] which is reproduced herein as Fig 2. The open circle data points are molar volumes calculated from direct PVT measurements by NIST [3] and then graphically compared to those calculated from the indicated EOS choices. It is clear that the best fit amongst the EOS so examined come from the EOS labeled Spycher *et al*. (2003) {4]. However, it is also clear that the other classic EOS break down in their successes for predictions at pressures as low as 80 bars (8 x 10^6 Pa), and even the Spycher EOS is not 'proven' beyond 600 Bars (6 x 10^7 Pa). Many additional studies are underway in such labs as Duan *et al*., [5]. Most of these EOS are achieved by computer- template fitting of observed data and the theoretical explanations for the non-ideal properties of CO_2 are still evolving.



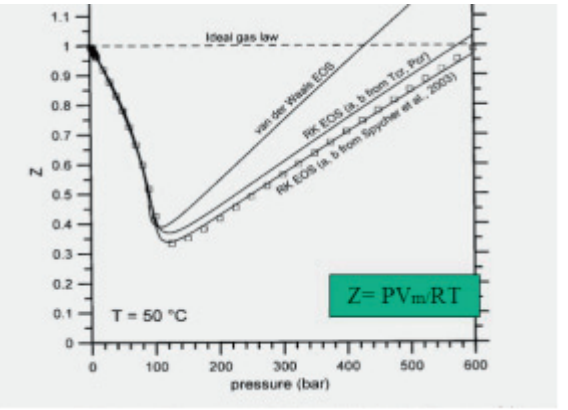


Fig. 1. (left) Schematic PT diagram for CO_2.

Fig. 2. (right) The compressibility, Z, of CO_2 computed from indicated EOS.

3. Fugacity Values Derived from EOS

Examining the published data from [6] (Fig 3.5 b, p 37) one can extract some isothermal and isobaric values for the fCO_2. The Marini fCO_2 data [6] do show that the fugacity of CO_2 may isobarically double in value with an increase of T of 100°C and may isothermally double in value with an increase of P of 400 bars (l0^7Pa) and overall this is good news in that deeper sequestration will benefit by these increased fugacities. However, the values of fCO_2 derived form EOS are variable, depending on which EOS is applied and the variations even between the most tested/trusted EOS range by as much as 25%. So any sequestration design predictions may also have considerable variations of observed data and the theoretical explanations for the non-ideal properties of CO_2 are still evolving.

4. Infrared Spectra of CO_2 at High P and T

To attempt to understand the non-ideality of the PVT CO_2 relationships many investigators have turned to IR spectral analyses of CO_2 at high P and T. Among these labs have been Tödheide and Franck [7] in their high pressure cells at the physical chemistry labs at Karlsruhe in Germany and Bodnar and Sterner in their works [8 & 9] at several labs on fluid inclusions in natural crystals. The use of IR spectra

at high P and T for CO_2 allows molecular models to be compared with expected/allowed molecular vibrations and their energy absorptions. By also invoking quantum mechanics, one may test various assumptions: do the observed wavelengths (energies) of observed absorptions 'match' the expectations of the proposed geometry of a given molecular model?

5. The Structure of CO_2 Gas

Even at sub-critical conditions, the many observed CO_2 property changes may point to some pressure-dependent molecular structure change. These suggestive evidences include non-ideality of CO_2 gas behavior (see above), the IR spectral changes with increases in P and T causing shifts in existing absorptions or loss or new bands in the spectra. And in a later section, the Joule Thomson coefficient change at about 10 bars also suggests that structural changes in the molecule are involved. At super critical pressure (~9 Kbars) Franck and Tödheide [7] (and a personal demonstration in their lab) found that a reversible photo-ionization is present in CO_2 that would correlate with a more polar CO_2 molecule at higher pressure. All these property changes raise the question of whether CO_2 is reliably as simple as the physical-chemistry-assumed linear molecule: a central carbon with two covalently bonded oxygens, all in a linear array at 180? Such a molecule would be only very weakly polar. Moreover, if this linear structure is pressure sensitive and invoked to explain such property changes, at what pressure do these molecular structural changes begin ?

6. The Joule Thomson Coefficients for CO_2

Well known to the refrigeration industry is the fact that compressed CO_2 allowed to expand from about 10 bars(10^6 Pa) will cool as it expands to ambient pressure and this phenomenon is defined formally as $\delta P/\delta T$, the Joule Thomson coefficient, which in 'easy language' defines how the temperature changes as the pressure is changed? In this cited case, the JT coefficient is one that mathematically will register in the heat balance as a cooling.

Unfortunately there is no global unification as to the sign convention, *i.e*, positive or negative, that is, or should be assigned to a cooling phenomenon. This fact has created much confusion in literature data bases. Therefore one working in this area of science needs to be sure which convention is involved. Is a positive coefficient linked to cooling or heating?

The JT aspects for CO_2 are even more unusual: the truth seems to be emerging into the general literature that a CO_2 expansion actually changes from cooling to heating, depending on the starting pressure: in general, an expansion starting from above 10 bars causes a heating, while an expansion starting from below 10 bars causes a cooling. The need to point out this confusion immediately is obvious when one looks to the JT data bases for CO_2. Very well respected data sources such as the International Critical Tables, the International Engineering Tables, and more recently (2003) the NIST Standard Reference Web Database #69 do not agree on the JT properties of CO_2, even at the same choices of P and T ! The disagreement may likely arise from the sign convention confusion: Is the expansion from a given starting pressure a cooling or a heating? It seems to depend on what pressure is involved.

Thus for CO_2 there is double-barrel possible confusion: that of the assignment of algebraic sign and that of an unusual reversal in the JT coefficient for CO_2. Marini [6] and Andrews [10] and Sirkis [11] all from different fields of study have all shown that CO_2, when expanded from above 10 bars will produce a heating and when expanding below 10 bars will produce a cooling. This phenomenon is still being integrated into sequestration planning and possible heating or cooling effects involved with ground water.

7. Metamorphic Facies

In the field of metamorphic, there is a host of specific studies and even textbooks that establish that down the geothermal gradient, the carbonation-decarbonation reactions will not take up CO_2, but rather evolve it. Indeed at the lower P and T regime of weathering there is again abundant literature that discusses the reaction of CO_2 to become 'fixed' as produced, by-product carbonates. The confusion in examining these two bodies of literature arises in the choice of what P and T are invoked for the carbonation/decarbonation reactions in sequestration schema. For example:

$CaCO_3 + SiO_2$ [siliceous limestone] = $CaSiO_3 + CO_2$ [Pyroxene and gas]

represents prograde metamorphism , but in the reverse sense could represent weathering of a silicate in a bicarbonate-driven environment in the classic Goldich-sense [12] (1928 *et sequitur).* However, recalling that many sequestration target sites are deep wells or mines means that a literature review of the both the weathering studies at shallow P and T and of the metamorphic literature at deeper geothermal gradient P and T values needs to be integrated in sequestration overall designing. Key authors in the metamorphic lab studies include Lüttge and Metz [13] and Lüttge *et al* [14] whose works examine the P and T and mole fractions of H_2O/CO_2 as the critical variables in such carbonation reactions. Several classic textbooks thoroughly examine the PT phase diagrams of the carbonation reactions [15-16].

8. Lake Nyos: What can we learn from this natural event?

In the Cameroon of Africa, a tragic outpouring of gases from a caldera lake in 1986 killed many humans and animals as the heavier than air gases released from the lake's waters overflowed the caldera rim and poured down the flanks of the mountain suffocating all life that was not taller than about 4 feet above the slope. While Giggenbach [17] did not find CO gas (below his detectability) in the water, the idea must be examined that CO may have bubbled through the water in which it is not very soluble, and accordingly built up over time in the 'stagnant' overlying heavy layer of atmosphere inside the caldera rim. Equilibria calculations [18] would indicate that there was a likely presence of CO and possibly graphite if the CO_2 was volcanically produced. So a lesson about sequestration at deep geothermal conditions should be to be sure to anticipate the possibility of the presence of CO and hence monitoring should be considered for any CO leakage that may be involved. Even parts per million of CO are lethal.

9. Conclusions

The critical designing of sequestration planning must achieve the permanent storage of the injected CO_2. Figure 3 schematically shows what the successful plan has to achieve: to have some idea of the post-injection time needed until the CO_2 will be self-contained, requires a better understanding of even the sub-critical properties of CO_2, as this article has discussed.

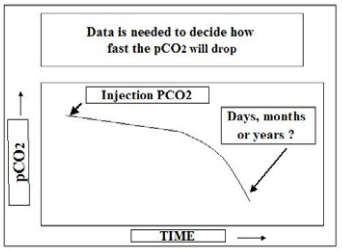


Fig. 3. Timing of successful sequestration.

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